On the Structure of a Proposed Mixed-Valent Analog of the Diiron Subsite of [FeFe]-Hydrogenase

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Electronic Supplementary Information (ESI):

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2. IR spectra of 2D.
3. Spectral subtraction of the solution spectrum of 2D.
4. Spectroelectrochemistry of [Fe₂(μ-S(CH₂)₂S)₂(CO)₃(NCCH₃)]²⁻, 2A.
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1. Synthesis of $[\text{Fe}_4(\mu-\text{S}(\text{CH}_2)_{2}\text{S})_2(\mu-(\text{CO})_2\text{CO})_8]^{2-}$, 2D.

All operations were performed under strictly anaerobic conditions. A small excess of Li[HBEt$_3$] (100 mM in THF, 145 µL) was added dropwise to a solution of Fe$_2$(µ-S(ÇH$_2$)$_2$S)(CO)$_5$(NCMe), 2A$_{\text{CO}}$ (0.05 g, 0.134 mmol) in ca. 5 mL THF. This was accompanied by a change in the colour of the solution from orange/red to black. A solution of NEt$_4$Cl (0.025 g, 0.15 mmol) in CH$_3$CN was added and the mixture left to stand at room temperature whereupon large black prismatic crystals of [NEt$_4$]$_2$ 2D formed over the period of ca. 10 days. The yield of the air-sensitive compound was estimated to be ca. 40%. The homogeneity of the sample was confirmed by IR spectroscopy and the structure of 2D determined by X-ray crystallography. IR (solid, KBr): $\nu$(CO) 1978 (s), 1917 (s), 1910 (sh), 1872 (m) and 1674 (m) cm$^{-1}$. IR (CH$_3$CN): $\nu$(CO) 2053 (w), 2042 (w), 1978 (s), 1917 (s), 1872 (vw) and 1700 (w) cm$^{-1}$.

2. IR spectrum, in the $\nu$(CO) region, of 2D dispersed in KBr.

The solution IR spectrum of 2D differs from that obtained from solid state samples in terms of the wavenumber and breadth of the bridging CO band, which may readily be explained in terms of differing ion pairing interactions, and the breadth of the 1872 cm$^{-1}$ band, which may reflect some conformational flexibility of the tetranuclear molecule in solution.
3. Spectral subtraction of the solution spectrum of 2D.
4. Spectroelectrochemistry of $[\text{Fe}_2(\mu-S(CH_2)_2S)_{23}(CO)_{5}(NCCH_3)]^{2-}$, 2A.

Reflection absorption IR-SEC results obtained for dinitrogen-saturated solutions of 2D (1 mM in CH$_3$CN, 0.2 M [N(Et)$_4$][ClO$_4$]). Spectra were recorded with an interval of 1.5 s following (a) reduction and (b) reduction. The bolded trace corresponds to the last recorded for the series. The IR-SEC cell has previously been described; the electrodes comprised highly-polished 3 mm diameter vitreous carbon disc working electrode, silver pseudo-reference and platinum foil counter where a PAR model 362 scanning potentiostat was used to control the potential applied to the cell.
5. Spectral deconvolution of the spectroelectrochemical product.

Absorbance spectrum of the product obtained following reduction of $2\text{A}_{\text{MeCN}}$ in SEC experiments. The sample of $2\text{A}_{\text{MeCN}}$ is contaminated by a small amount of the parent hexacarbonyl, $2\text{A}_{\text{CO}}$, and the depletion and growth bands associated with this compound and reduction products are evident in the spectra between 2000 and 2100 cm$^{-1}$. 

[Graph showing absorbance spectra with annotations for DA, SM, and K0]
6. Description of the structure of 2D.

The coordination environment about the four iron atoms of 2D is square pyramidal (or \( \psi \)-octahedral, with the bent M-M bond the electron pair) and has a core geometry analogous to that reported for Fe4[MeC(SCH2)3]2(CO)8, 4Fe6S.\(^2\) For 4Fe6S the diiron units are linked by bridging thiolato groups. The core geometry involving pairs of thiolate (or phosphido) bridged bimetallic units that are connected by a M-M bond supported by bridging ligands is otherwise unprecedented within iron-sulfur chemistry. The arrangement of terminally-bound CO groups of each diiron fragment of 2D and 4Fe6S matches that of the crystallographically-characterised apical-basal isomers of Fe2(\( \mu \)-S(CH2)3S)(CO)4(PP), PP = PPh2(CH2)2PPh2 \(^3\) or PPh2(CH)2PPh2, \(^4\) and in each of these cases a similar pattern IR-active terminal-\( \nu \)(CO) bands is obtained. The three Fe-Fe contacts of 2D are in the range 2.53 to 2.57 Å and this indicates Fe-Fe bonding interactions both within and between the CO-bridged diiron units as would be consistent with a formal Fe\(^{I}_{4}\)Fe\(^{0}\)Fe\(^{0}\)Fe\(^{I}\) oxidation state assignment. It is interesting to note that for 4Fe6S the Fe-Fe distances are longer (2.54-2.63 Å) despite the Fe\(^{I}_{4}\)Fe\(^{II}_{2}\)Fe\(^{II}_{2}\)Fe\(^{I}\) formal oxidation state assignment. The terminal-\( \nu \)(CO) band profile of 2D is shifted by 69±2 \( \text{cm}^{-1} \) lower than that of 4Fe6S, consistent with the higher oxidation state assignment for the latter although it is noted that this magnitude of shift of the CO frequencies is similar to that obtained by one-electron reduction of 4Fe6S.\(^5\)

7. References